ELSEVIER

Polymer 40 (1999) 5741–5749

polymer

Interactions between the nonionic surfactant and polyacrylamide studied by light scattering and viscometry

Khine Yi Mya[a], Alexander M. Jamieson[b], Anuvat Sirivat[a,*]

[a]The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
[b]Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH, USA

Received 9 June 1998; received in revised form 3 November 1998; accepted 3 November 1998

Abstract

Light scattering and viscometric measurements were made on ternary mixtures of high molecular weight polyacrylamide (PAM), and the nonionic surfactant, Triton X-100 (TX-100) in aqueous solution. The binary solutions of polymer and surfactant in aqueous media were also studied. In the ternary system, the solution viscosity and translational diffusion coefficients were determined at 30°C in terms of (a) the surfactant concentration at fixed PAM concentration, (b) the PAM concentration at fixed surfactant concentration, and (c) the PAM molecular weight. The surfactant concentration was varied by five orders of magnitude, the mean diffusion coefficient decreased slightly at first until reaching a minimum and then rose toward an asymptotic value which was identical to that of a single micelle. Near the cmc, the binding of the surfactant onto a polymer chain induced a slight chain expansion, but surprisingly the specific viscosity diminished. DLS shows a component owing to free micelle diffusion at concentrations above 1 mM of TX-100. This indicates the saturation point of binding between PAM and TX-100. Different molecular weights of PAM interacted with the surfactant quite similarly. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyacrylamide; Triton X-100; Dynamic light scattering

1. Background

The interaction between polymers and surfactants was the subject of intense research effort, because of both fundamental and technological interest. Understanding of polymer–surfactant interactions is relevant to important industrial and biological processes, for example, polymers and surfactants are used conjointly in enhanced oil recovery [1]. In addition, polymer–surfactant systems are widely used in cosmetics formulations, in the food industry and in paints [2]. Most studies in this field focus on complexes of anionic surfactants (generally sodium dodecyl sulfate and its homologs) with polymers such as poly(ethylene oxide) (PEO) [3,4], poly(propylene oxide) (PPO) [5]. These studies indicate a strong interaction between polymers and anionic surfactants whereas cationic surfactants (generally alkylammonium salts) [6] are found to interact weakly. If the hydrophobic character of the polymer is increased, a more pronounced interaction can be observed with cationic surfactants. For example, complex formation was reported between hydroxypropyl cellulose (HPC) and hexadecyltrimethylammonium chloride (HTAC) micelles [7], and between ethyl(hydroxyethyl) cellulose (EHEC) and *N*-tetradecylpyridinium bromide (TDPB) [8].

The interaction between an uncharged polymer and an uncharged surfactant is generally considered also to be very weak e.g. various polymers show no interaction with polyethoxylated nonionic surfactants [9]. Recently, some studies suggest that there is a significant interaction in aqueous neutral polymer and nonionic surfactant systems. Boscher et al. [10] observed evidence for an interaction between polyethylene oxide nonyl phenyl ether, and hydroxyethylcellulose (HEC) by light scattering measurements. Szmerekova et al. [11] reported interaction activity between nonylphenol polyethylene glycol and PEO using gel permeation chromatography. Brackman et al. [12] described the formation of a polymer–micelle complex of poly(propylene oxide) (PPO), with *n*-octyl thioglucoside (OTG). The occurrence of PPO–OTG association was confirmed by microcalorimetric measurement, although the cmc in the presence of polymer was identical to that of the pure surfactant. Winnik [13] reported an interaction between pyrene-labeled hydroxypropyl cellulose (HPC) and OTG using fluorescence measurements. Zhang et al. [14], described self-diffusion measurements on solutions of ethylhydroxyethyl cellulose (EHEC), containing the nonionic surfactant,

---

* Corresponding author.

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00811-8

$C_{12}E_8$, micelles, and found that the micelle diffusion was influenced by the polymer in two ways; obstruction owing to the polymer network and association of micelles to the polymer chains.

Feitosa et al. [15] studied the interaction between PEO and $C_{12}E_5$ using dynamic light scattering and fluorescence quenching methods. These authors observed a significant increase in the aggregation number of the $C_{12}E_5$ micelles with increasing polymer concentration leading to the formation of a complex made up of clusters of surfactant micelles stabilized within the polymer coil. Also, the cmc in the presence of the polymer was found to be the same as in water, in contrast to the lower cac value typically observed when ionic surfactants interact with neutral polymers. As further evidence for the existence of neutral polymer/surfactant complexes, we present light scattering and viscometric data on the association of polyacrylamide (PAM) with micelles formed from the nonionic surfactant Triton X-100 (TX-100).

2. Experimental section

2.1. Materials

Two different molecular weights of polyacrylamide (PAM) [PS-19901 $= 7 \times 10^5 M_w$, PS-02806 $= 5 \times 10^6 M_w$] were obtained from Polysciences Inc. Commercial grade Triton X-100 (TX-100) was used as a nonionic surfactant, obtained from Union Carbide, Thailand Ltd. Each material was used without further purification. Sterile water was purchased from Thai Pharmaceutical Organization. Before use in light scattering experiments, it was filtered through 0.2 μm Millipore membrane filters. Analytical grade sodium azide (NaN_3) from Clyde Industries Ltd., was added to prevent the growth of microorganisms in polyacrylamide solutions.

2.2. Preparation of PAM-Triton X-100 solutions

Dilutions of PAM and TX-100 stock solutions were performed by adding calculated amounts of solvent. The complex solutions were prepared by adding prefiltered diluted PAM solutions to diluted TX-100 solutions. The solutions were stirred slowly at room temperature for at least 24 h, and then allowed to equilibrate overnight before use. Prior to each DLS and viscometric measurement, the sample solutions were centrifuged at 8000 rpm for 1 h and then filtered through Millipore filters (pore sizes 0.22, 0.45, and 0.8 μm depending on the concentration and molecular weight).

2.3. Dynamic light scattering

Dynamic light scattering (DLS) experiments were performed with a light scattering apparatus from Malvern Instruments (Model 4700), with an Argon laser source (wavelength $\lambda = 514.5$ μm). DLS measurements were made at a scattering angle of 90° with a 200 μm pinhole to obtain the homodyne intensity–intensity correlation function $g^{(2)}(q,t)$. For a Gaussian distribution of intensity profile of the scattered light, $g^{(2)}(\tau)$ is related to the first-order electric field autocorrelation function $g^{(1)}(\tau)$ through the Siegert relation:

$$g^{(2)}(\tau) = A\Big(1 + B\Big(g^{(1)}(\tau)^2\Big)\Big), \tag{1}$$

where A is the experimental baseline and B is the coherence factor. The normalized time correlation function $g^{(2)}(\tau)$ of the scattering intensity $I(q,\tau)$ is defined by the following equations:

$$g^{(2)}(\tau) = \frac{\langle I(q,0)I(q,\tau)\rangle}{\langle I(q,0)\rangle^2}, \tag{2}$$

where

$$g^{(1)}(\tau) = \exp(-\tau/\tau_q), \tag{3}$$

and q is the scattering wave vector,

$$q = (4\pi n/\lambda)\sin(\theta/2). \tag{4}$$

λ and θ are the wavelength of the excitation light in vacuum and the scattering angle respectively. The decay rate of the correlation function (Γ) is directly related to the z-average self-diffusion coefficient of the polymer in solution (D_t),

$$\Gamma = 1/\tau_q = D_t q^2. \tag{5}$$

In the present work, we obtained the decay rate distribution function by the Pike–Ostrowsky exponential sampling method in which $g^2(\tau)$ is sampled at a series of exponentially-spaced sample times. The procedure is automated to determine the best fit in an iterative process. First, the cumulant result is checked to see if the polydispersity exceeds a certain threshold (normally 0.05), in which case a set of exponential sampling analyses of reducing width are then tried until the fit error no longer improves.

For a polydisperse polymer, the z-average diffusion coefficient is obtained from the mean decay rate Γ, via Eq. (5). The z-average translational diffusion coefficient, D_t, indicates the size and the structure of particles in solution in the form of the apparent hydrodynamic radius, $R_{h,app}$, which is obtained using the Stokes–Einstein equation,

$$R_{h,app} = k_B T/6\pi\eta_s D_t. \tag{6}$$

A bimodal distribution of relaxation rates was measured to evaluate and to discuss the effect of surfactant; we will present data only on the slow mode which contains most of the scattered intensity and whose relexation rate is numerically consistent with expectation based on the literature value for the diffusion coefficient of PAM [16]. The fast mode has too short a relaxation time to correspond to translational diffusion and is presumed to be because of the internal relaxation mode.

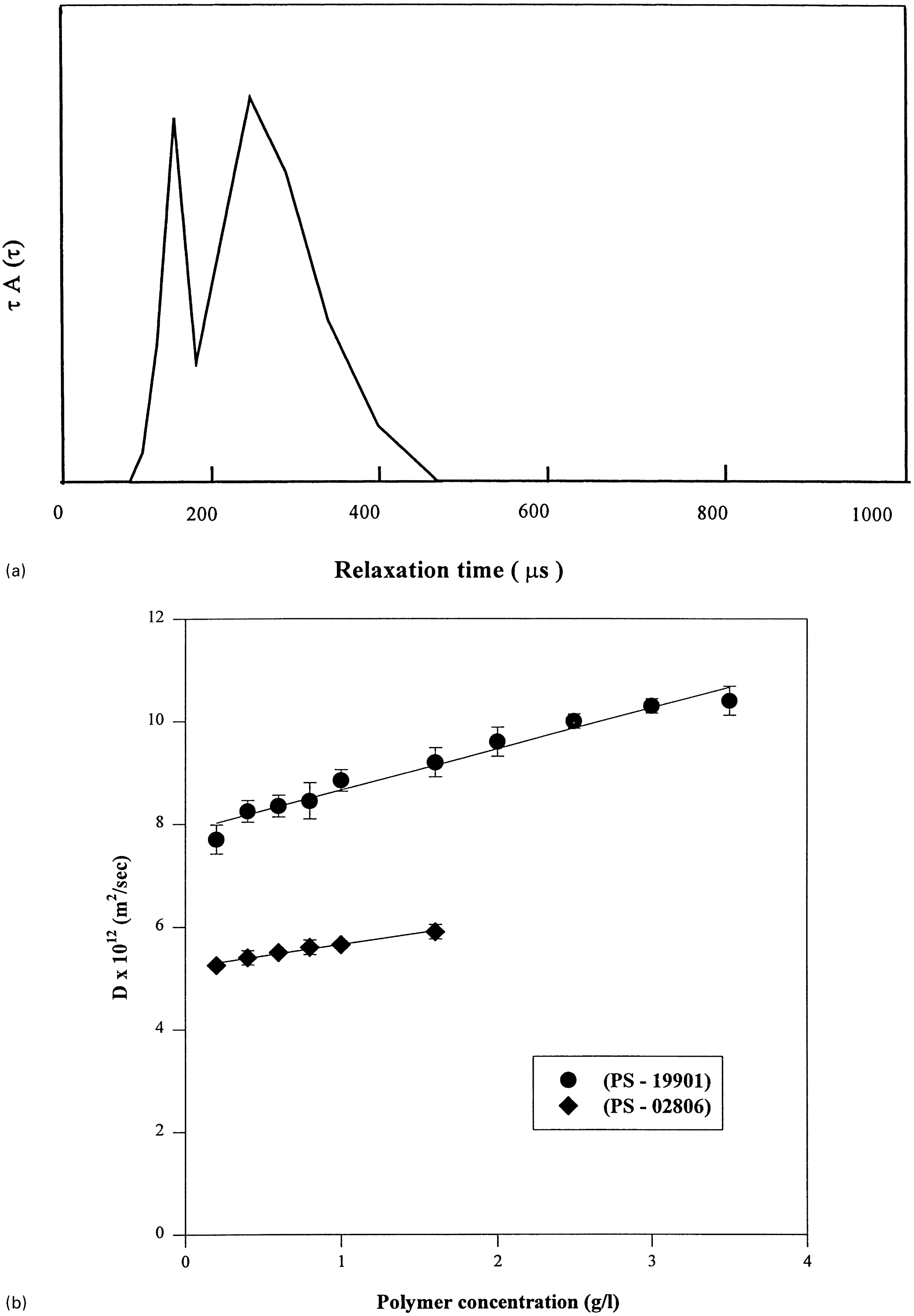

Fig. 1. (a). Relaxation time distribution for 0.4 g l^{-1} PAM solution. (b). Diffusion coefficients of PAM of different M_w as a function of concentration.

Table 1
Physical properties of PAM in aqueous solutions

Sample	M_w (g mol^{-1})	$D_0 \times 10^8$ (cm^2/s)	R_h (nm)	$[\eta]$ (ml/g)
PS-19901	699 000	7.84	35.37	260.30 ± 15
PS-02806	2 560 000	5.22	53.12	700.97 ± 50

2.4. Viscosity

Viscosity measurement is a convenient tool to study the hydrodynamic volume of polymers in the solution. The viscosity of a polymer solution is dependent on both concentration and on the average molecular size of the sample and hence the molecular weight.

For the viscosity measurement, an Ubbelohde viscometer was used and the apparatus was thermostatted at 25 ± 0.05°C. The reduced viscosity (η_{red}) of the polymer was calculated from the following equation:

$$\eta_{red} = (\eta - \eta_0)/\eta_0 c, \tag{7}$$

where η and η_0 are the viscosities of the polymer solution and the solvent, c is the polymer concentration expressed in g l^{-1}. The intrinsic viscosity was determined by extrapolation of the reduced specific viscosity

$(\eta_{sp} = \eta_r - 1)$

to zero concentration using the Huggins equation:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c + \cdots \tag{8}$$

However, interpretation of the reduced viscosity in ternary system of PAM/TX-100/ water is not straightforward because of the possible coexistence of polymer, micelles and polymer–miscelle complexes. Therefore, we present data on the specific viscosity for ternary systems instead of the reduced viscosity.

3. Results and discussion

3.1. Binary systems

Fig. 1(a) shows a typical DLS relaxation time distribution at scattering angle $\theta = 90°$ for PAM (7×10^5 M_w) in water at 30°C at a concentration of 0.4 g l^{-1}. This analysis indicates a bimodal distribution. The fast mode is presumed to be because of internal relaxation of polymer chains. The slow mode corresponds to center of mass diffusion. Plots of the translational diffusion coefficient vs. concentration for two different molecular weights are shown in Fig. 1(b). The diffusion virial coefficient, k_D, describes the concentration dependence of the diffusion coefficient as

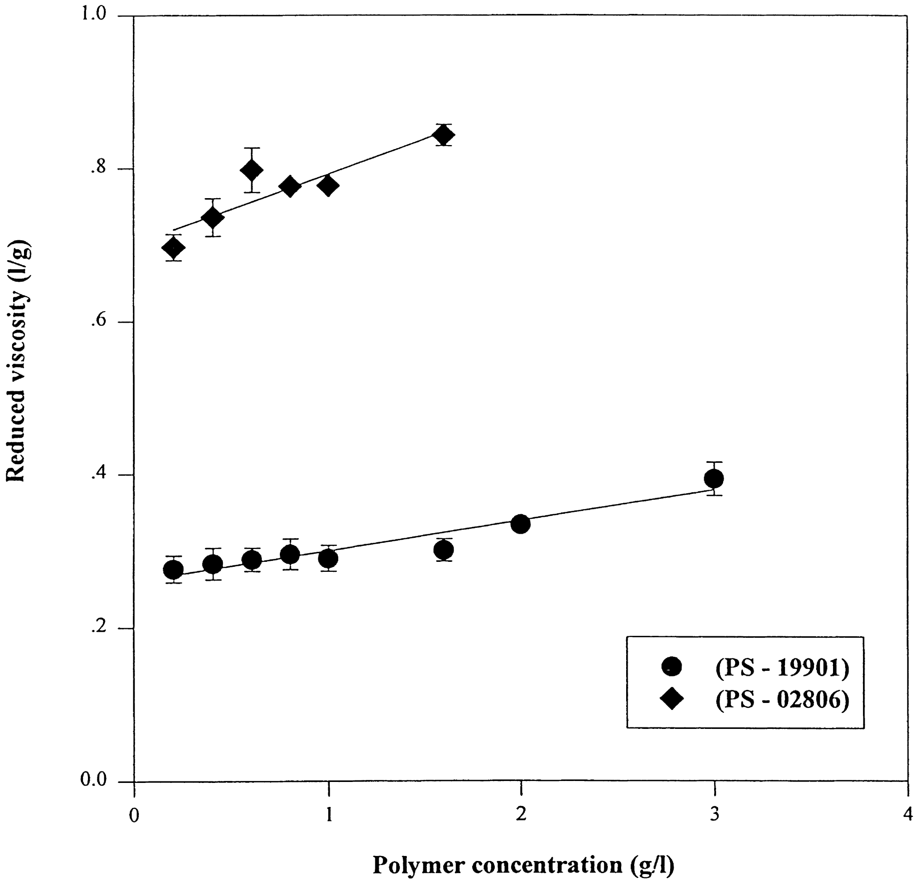

Fig. 2. Reduced specific viscosity vs. concentration for PAM in water.

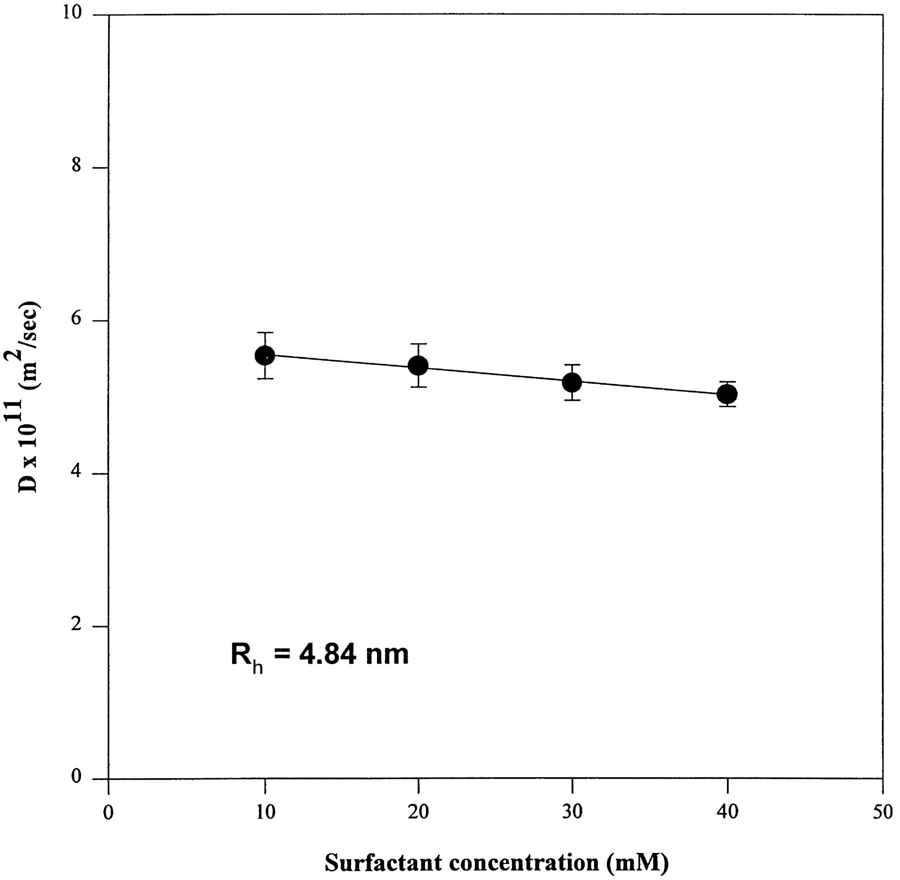

Fig. 3. Diffusion coefficient of TX-100 micelles in water as a function of concentration.

$$D_t = D_{t,0}(1 + k_D c),$$
$$k_D = 2A_2M - k_f - v_2, \tag{9}$$

where A_2 is the second osmotic virial coefficient, k_f is the concentration dependence of the frictional coefficient and v_2 is the partial specific volume. As water is a good solvent for PAM, the second virial coefficient A_2 is large and positive, and therefore D_t increases with increasing polymer concentration. At infinite dilution, the hydrodynamic radius R_h for each polymer was calculated using the Stokes–Einstein equation (Eq. (6)). The results are shown in Table 1.

Fig. 2 shows the reduced viscosity for PAM of two different molecular weights vs. PAM concentration. The plots yield the intrinsic viscosity from the intercept and the Huggins constant from the slope of the best line through the experimental points according to Eq. (8). Table 1 summarizes the experimental results of molecular weight, diffusion coefficient, R_h and intrinsic viscosity. Within experimental errors, our diffusion results are consistent with the values reported by Patterson et al. [16] for polyacrylamide on 0.1 M NaCl at 20°C, and the intrinsic viscosity data are in agreement with values deduced from the study of Klein [17].

Fig. 3 shows the diffusion coefficient of Triton X-100 (TX-100) micelles as a function of concentration, in the range $10 \leq C \leq 50$ mM, 10 mM being the lowest surfactant concentration at which high quality spectra of the micelle solution could be obtained. The diffusion coefficient extrapolated to the cmc of Triton X-100 (0.18 mM) was used to calculate the hydrodynamic radius according to Eq. (6) and the value of R_h of 4.84 nm at 30°C was obtained. This value is in good agreement with the value reported by Phillies [18].

3.2. Ternary system

3.2.1. cmc measurement

Surface tension measurements of the cmc were performed by using the Dunuay ring method. We found that the cmc in the presence of polymer is identical to that of the pure surfactant. This is in agreement with the observation of Brackman [12] on a different nonionic polymer and nonionic surfactant solution.

3.2.2. DLS measurement

To study the interaction between surfactant and polymer, the polymer concentration was fixed at 0.4 g l^{-1} and the surfactant concentration was varied in both DLS and viscometric experiments. Fig. 4(a) shows the DLS relaxation time distributions for a solution containing 0.4 g l^{-1} of PAM with

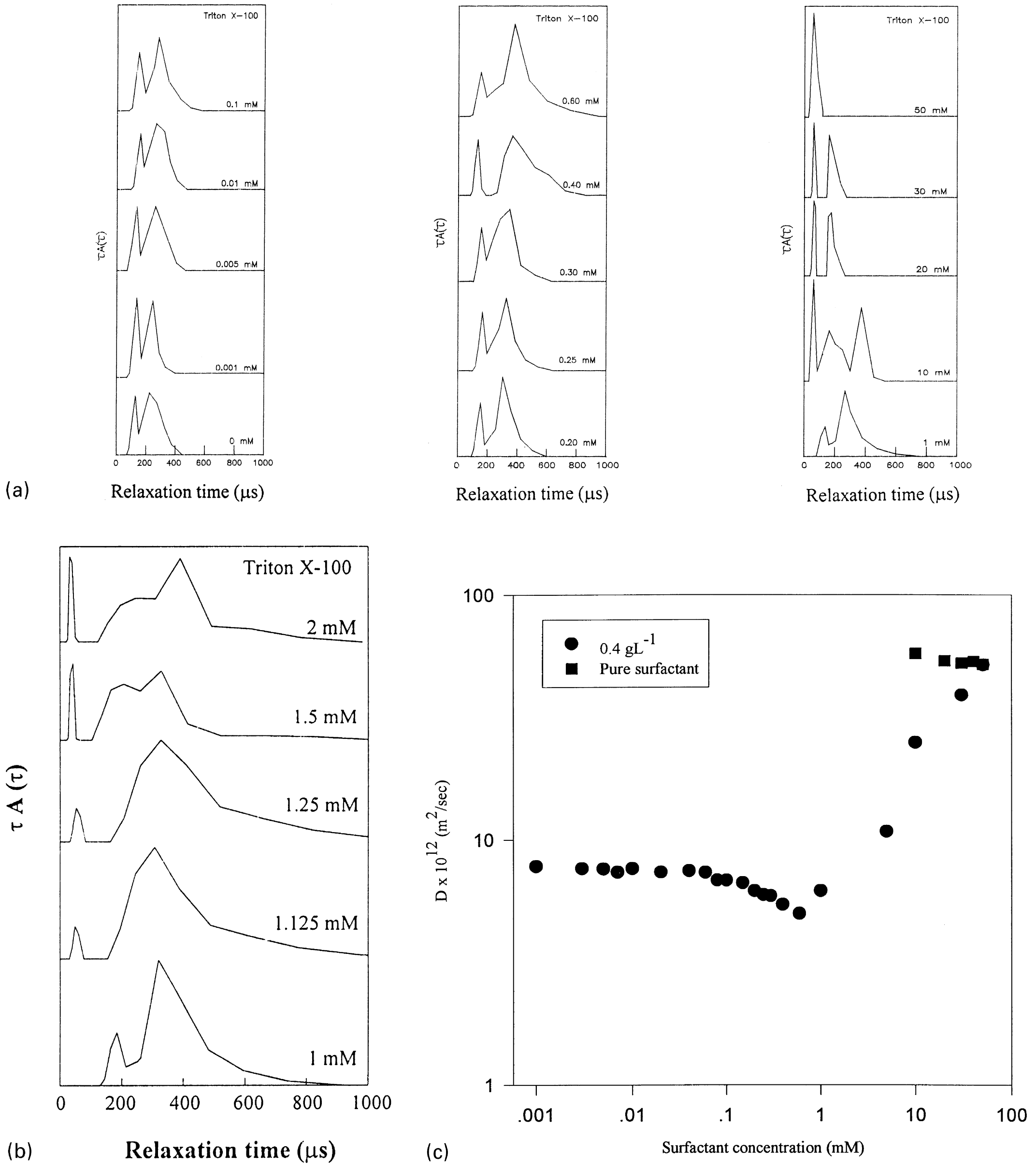

Fig. 4. (a). Relaxation time distribution for 0.4 g l^{-1} PAM solutions with successive increases in TX-100 concentration. (b). Relaxation time distributions for 0.4 g l^{-1} PAM solutions within a narrow concentration range of TX-100. (c). Diffusion coefficient vs. TX-100 concentration for 0.4 g l^{-1} PAM solutions.

successive increases in Triton X-100 concentration at 30°C. Bimodal distributions were observed for the mixtures at low surfactant levels, and an increase in the slow mode relaxation times with the increase of the surfactant concentration is clearly evident. The fast mode has an approximately constant relaxation time while the slow mode is displaced to longer relaxation times as surfactant concentration increases. The fast mode corresponds to the internal relaxation of polymer chains and the slow mode is attributed to diffusion of complexes consisting of surfactant micelles bound to the polymer coil. Addition of Triton X-100 has relatively little effect until its concentration exceeds 0.1 mM. Then it induces a shift toward longer relaxation times until the concentration of 1 mM is reached. These changes occur very clearly over the narrow surfactant concentration range of 0.1–1 mM, that is, near and just above the cmc of Triton X-100 (0.18 mM). A similar phenomenon was found in the interaction of fluorescent dye labeled HPC with the nonionic surfactant *n*-octyl β-D-glucopyranoside (OG) reported by Winnik [13]. It was shown that the interaction occurred over a narrow OG concentration range of 2.5×10^{-2}M (just above the cmc of OG). Above 1 mM, as shown in Fig. 4(b), a very fast mode appears owing to diffusion of pure surfactant micelles whose intensity increases with increasing surfactant concentration. At very high surfactant concentration of 50 mM, only a single mode is observed with relaxation time identical to that of the pure surfactant micelles. From the DLS

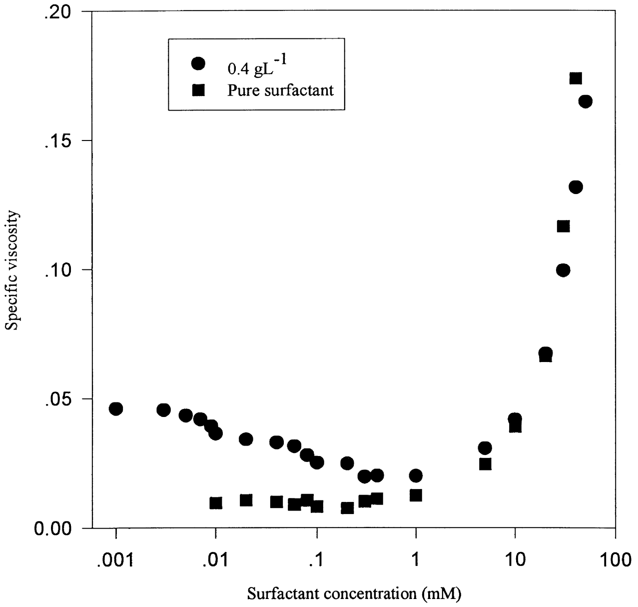

Fig. 5. Semi-logarithmic plot of the dependence of the specific viscosity of TX-100 concentration for 0.4 g l^{-1} PAM solutions.

results, we conclude that the binding of surfactant micelles to polymer chains are saturated above 1 mM of surfactant concentration. Fig. 4(c) presents the diffusion coefficients obtained from the relaxation rate distributions in Fig. 4(a) as a function of surfactant concentration and we compare them against the diffusion coefficient of pure surfactant solution. The results are consistent with the expectation that, adding the surfactant to the polymer solution, adsorption of the surfactant molecules to the polymer chain occurs. Near the cmc value, the binding of the surfactant molecules to the polymer chain induces a slight chain expansion. Above 1 mM, there appears to be a small contraction of the PAM chain or a diminution of complex aggregates. Possibly, there is some screening of the chain excluded volume effect as excess micelles are added, analogous to the situation in complexes formed between HPC and charged micelles. At very high surfactant concentration, D_t is identical to that of a single surfactant micelle. In this concentration range, the number of micelles is sufficient and that light scattered is dominated by the surfactant micelles.

3.2.3. *Viscosity measurement*

Fig. 5 compares the specific viscosities of the PAM–surfactant complex solution and the pure surfactant solution as a function of surfactant concentration. As more surfactant is added to the solution, the viscosity slightly decreases until reaching a minimum value near 1 mM of surfactant. Physically, we can explain this result by the following:

$$\eta_{sp} = 2.5N_A V_h c/M = 2.5(\#\text{ of solute molecule})V_h, \qquad (10)$$

where V_h is the average hydrodynamic volume.

In Fig. 5, specific viscosity decreases initially. The diffusion data in Fig. 4(c) indicates that the hydrodynamic volume increases, it appears therefore, from Eq. (10) that the number of particles decreases. Therefore, we conclude that binding of the surfactant molecules to the polymer chains induces an aggregation of chains over the range of 0.1–1 mM of surfactant concentration., i.e. a reduction in the number of solute species. In this context, the decrease in R_h above 1 mM of surfactant may reflect dissociation of micelles near the saturation of binding. The subsequent increase in viscosity at very high surfactant concentration is suggested to be owing to the contribution from pure surfactant solution.

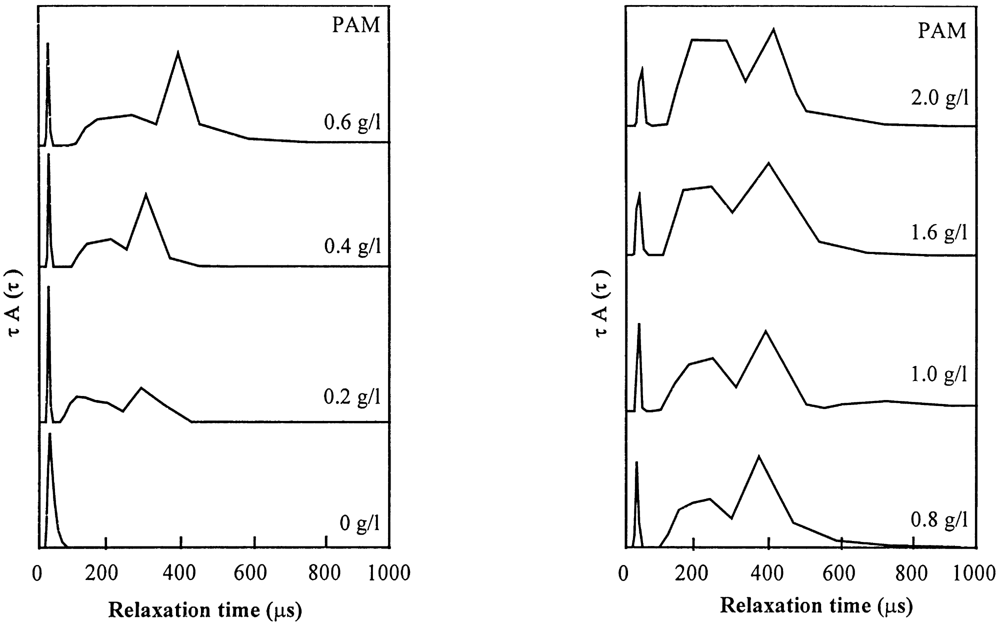

Fig. 6. Relaxation time distributions at various PAM concentrations.

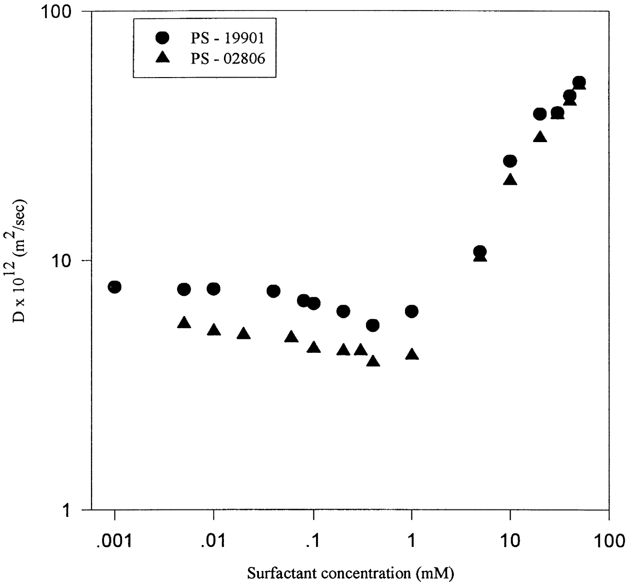

Fig. 7. Dependence of diffusion coefficient on surfactant concentration for 0.4 g l^{-1} PAM solutions of two molecular weights.

Fig. 6 shows the DLS relaxation time distributions for various concentrations of PAM at a fixed surfactant concentration (5 mM). The shortest relaxation time represents free surfactant micelles. The micelle mode intensity decreases with increasing polymer concentration. The intensities of the intermediate and slow modes, which refer to the internal motion and the polymer diffusion respectively, increase with increasing polymer concentration and their relaxation times also increase to a small extent, presumably owing to aggregate formation.

Fig. 7 shows the dependence of diffusion coefficient on surfactant concentration for two different molecular weights of polymer. This plot indicates a similar trend for the two different molecular weights, viz. a shallow minimum in D_t between 0.1 and 1 mM surfactant concentrations. Fig. 8 shows the specific viscosity of the complex solution for two PAM's of different molecular weights as a function of surfactant concentration. Again, this figure indicates similar behaviors for different molecular weights. Therefore we conclude that the polymer–surfactant interaction would appear to be the same for both molecular weights.

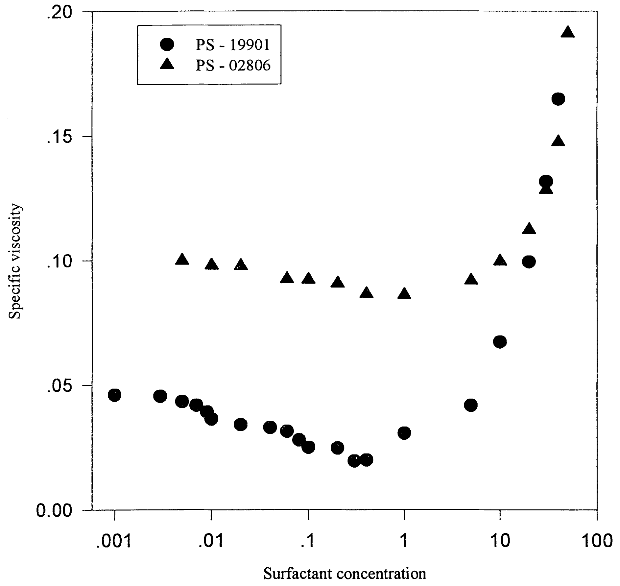

Fig. 8. Specific viscosity of 0.4 g l^{-1} PAM solutions at various TX-100 concentrations.

The mechanisms for complex formation between a neutral polymer with a nonionic surfactant interaction are different from the interaction between a nonionic polymer and an ionic surfactant. Shirahama et al. [19], proposed the pearl-necklace model of the neutral polymer with ionic surfactant complex according to which micelle-like aggregates are decorated along the polymer chain. Holmberg et al. [20], also proposed the site clustering model where the surfactant molecules cluster around the hydrophobic sites of the polymer. Another model, where the polymer segments only partially penetrate and wrap around the hydrophilic micellar surfaces, is called the mixed-micelle type structure. The latter model would appear to be most likely to describe complex formation between nonionic polymer and nonionic surfactant.

4. Conclusions

In the solutions of PAM containing sufficiently low concentrations of Triton X-100, both R_h and specific viscosity are independent of surfactant concentration. This indicates that no interaction between PAM and Triton X-100 occurs. Most of the surfactant molecules exist freely in the form of monomers. At higher concentrations the surfactant molecules induce a significant increase in the size of the polymer chains. This chain expansion occurs over a narrow Triton X-100 concentration range of 0.1–1.0 mM. Above this concentration, saturation of binding between polymer and surfactant occurs. To achieve self-consistent interpretation of DLS and viscosity measurements there must be an increase in the molecular weight of the polymer–surfactant complex in the narrow surfactant concentration range of 0.1–1.0 mM. Two polymers with different molecular weights interact with the surfactant quite similarly.

References

[1] Goddard ED, Ananthapadmanabhan KP. Interactions of surfactants with polymers and proteins. Boca Raton, FL: CRC Press, 1993.
[2] Mandel M. Encyclopedia of Polymer Science and Engineering, Vol. 3, New York: Wiley, 1985.
[3] Brown W, Fundin J. Macromolecules 1992;25:7192.
[4] Xia J, Dubin PL. J Phys Chem 1992;96:6805.
[5] Witte FM, Engberts JBJN. J Org Chem 1988;53:3085.
[6] Ruckenstein E, Huber G, Hoffmann H. Langmuir 1987;3:382.
[7] Winnik FM, Winnik MA, Tazuke S. J Phys Chem 1987;91:594.
[8] Carlsson A, Karlstrom G, Lindman B. J Phys Chem 1989;93:3673.

[9] Saito S. Polymer-surfactant interactions, in nonionic surfactants. In: Schick MJ, editor. New York: Marcel Dekker, 1987:881.
[10] Boscher FL, Quivoron C. Polymer Bull 1983;9:533.
[11] Szmerekova B, Kralik P. J Chromatography 1984;285:188.
[12] Brackman JC, van Os NM, Engberts JBFN. Langmuir 1988;4:1266.
[13] Winnik FM. Langmuir 1990;6:522.
[14] Zhang K, Jonstromer M, Lindman B. J Phys Chem 1994;98:2459.
[15] Feitosa E, Brown W, Hansson P. Macromolecules 1996;29:2169.
[16] Patterson PM, Jamieson AM. Macromolecules 1985;18:266.
[17] Klein J, Conrad KD. Makromol Chem 1980;181:227.
[18] Phillies DJ, Streletzky K. Langmuir 1995;11:42.
[19] Shirahama K, Himuro A, Takisawa N. Colloid Polym Sci 1987;265:96.
[20] Holmberg C, Nilsson S, Singh S, Sundelof LO. J Phys Chem 1992;96:871.